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Dispersion of electrolytic conductance in the frequency range (1MHz-6MHz) caused by ultrasonic wave propagation

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Electrolytic conductivity of magnesium sulphate solution at 25°C has been studied at various frequencies of ultrasonic waves. The experimental results show a marked and steep rise in the equivalent conductivity at some non relaxational frequency $\simeq 4$ MHz. It has been suggested that this marked rise in conductance may be due to the changes that occur in the relaxation mechanism leading to the disappearance of ionic atmosphere surrounding an ion in motion that otherwise retards the ionic mobility.

1. INTRODUCTION

The change in the conductance of an electrolytic solution as affected by ultrasonic disturbance has been studied by various workers (Roll 1951, Fox *et al* 1946, Altenberg *et al* 1952, Krishnamurthy 1951, Lichter *et al* 1948, Nolle 1949, Buonsanto 1951, Tumanabij *et al* 1939) from time to time, a few of them concentrating on the d.c. conductivity while others on the a.c. conductance. Some of the workers (Meyer 1936, Saidi 1940) have studied the effect of ultrasonic waves on the conductivity of organic liquids. Measuring all the frequency components associated with electrolytic current flow, recently Agarwal & Bhatnagar (1975, 1976) have reported a marked change in the electrolytic conductance of copper sulphate and silver nitrate solutions due to the propagation of ultrasonic waves.

It has been noted that the dispersion of conductance with frequency of ultrasonic waves has not been studied so far. To understand the mechanism by which the ultrasonic wave propagation interact with the ionic mobility, it was desired to collect data on the dispersion of conductivity with the frequency of ultrasonic wave propagating through electrolytic solutions. The authors therefore studied the dispersion of ultrasonic effect on electrolytic conductivity of magnesium sulphate aqueous solution, the results of which have been presented in the present paper.

2. EXPERIMENTAL ARRANGEMENT

To investigate the frequency dependence of ultrasonic effect an indirect method as described earlier Agarwal & Bhatnagar (1975, 1976) of launching ultrasonic waves in the solution has been used. In this setup ultrasonic waves

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are generated by a suitably mounted quartz crystal placed in compartment No. 1 containing insulating liquid and then they are allowed to penetrate through a thin plastic diaphragm to compartment No. 2 containing the experimental solution. The intensity of ultrasonic wave is controlled by controlling the r.f. voltage across the crystal. Ultrasonic waves of different frequencies were produced by vibrating piezoelectric crystals at their fundamentals. However to keep the acoustic power at the same level the voltage across them was adjusted accordingly.

The electrolytic conductivity was measured by noting the deflection in the galvanometer G which is a direct measure of the current flowing through the solution column maintained by two platinum electrodes of the size 2·19 cm (dia) separated at a distance of 1·37 cm. However, before recording the data the whole apparatus was calibrated with a standard solution of magnesium sulphate (Figure 1).

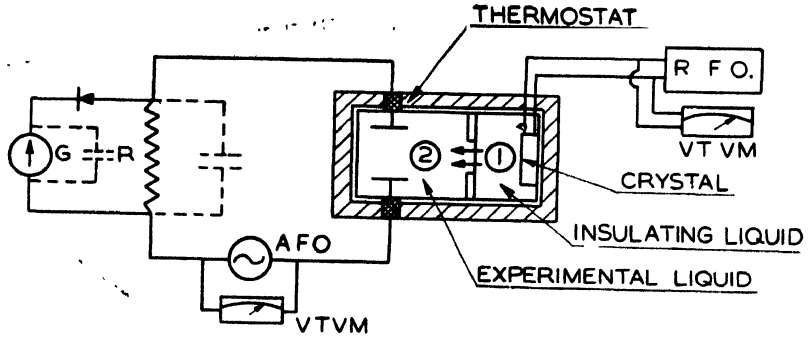

Fig. 1. Experimental set-up for conductivity measurements.

3. Results

In the absence of any external disturbance like pressure gradients maintained by ultrasonic waves, the equivalent conductivity of electrolytic solution at a particular temperature and concentration is constant; however it varies with concentration and attains maximum value at infinite dilution but as soon as ultrasonic waves are propagated in the medium a change in conductance is immediately observed. The change in conductance has been found to depend on the intensity and frequency of ultrasonic waves. To know the frequency dependence of the ultrasonic effect the equivalent conductivity was studied at various frequencies from 1 to 6 MHz keeping the acoustic power at the same level. The experimental results (Figure 2) show a marked rise and fall in the frequency region 1 to 6 MHz with a broad maximum arround 4 MHz. A change of similar nature has been observed and shown for the relative change in the dissociation constant ($\Delta\alpha/\alpha$) for varied concentration of the solution, as $\Delta\Lambda/\Lambda$

may be taken as $\Delta\alpha/\alpha$ where α is dissociation constant. The above results may also be interpreted to indicate the variation in $\Delta\alpha/\alpha$ with frequency of ultrasonic waves.

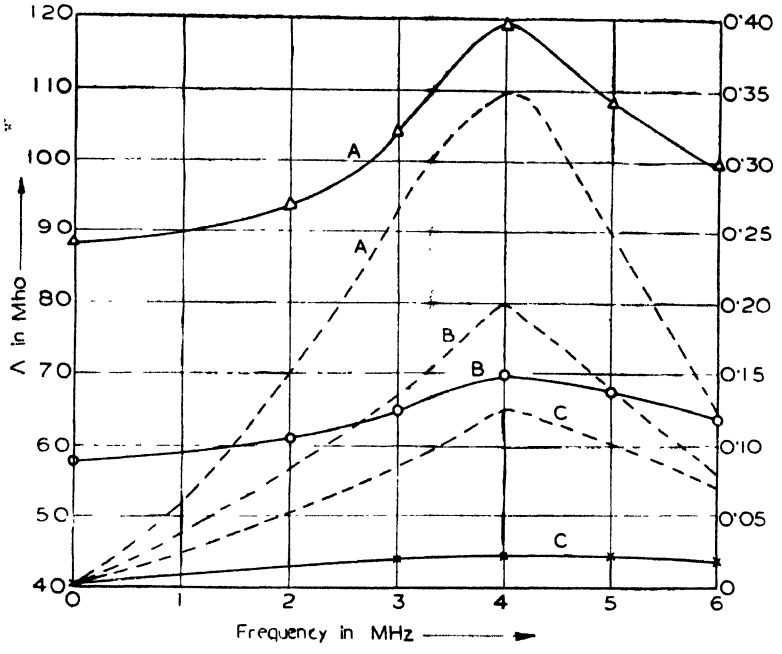

Fig. 2. Dispersion of electrolytic conductance of Magnesium Sulphate solution at 25°C. Curves A, B and C are for concentrations 0·01, 0·1 and 0·5 gm mol per lit. respectively. The dotted (- - - - -) curves stand for $\Delta\Lambda/\Lambda$ while continuous (——) curves show a variation of Λ. Frequency of a.f. oscillator, 400 Hz.

4. Discussions

The conductance of any electrolytic solution can be represented as the algebric sum of the conductance at infinite dilution Λ_∞, the conductance due to relaxational force Λ_I and conductance due to electrophoretic force Λ_Π i.e.,

$$\Lambda = \Lambda_\infty + \Lambda_I + \Lambda_\Pi. \quad \ldots (1)$$

When ultrasonic waves are allowed to pass through the solution, the conductance of the solution changes. This change in conductance may be attributed to

(i) The change due to interaction with the relaxational phenomena.

(ii) The change due to interaction with the electrophoretic effect.

Hence one can easily write

$$\Delta\Lambda = \Delta\Lambda_I + \Delta\Lambda_\Pi. \quad \ldots (2)$$

Here $\Delta\Lambda_I$ represents the change in conductance due to the change in the relaxational phenomena. From the results of Debye, Falkenhagen (Dole 1935) it is known that

$$\Lambda_I = \frac{eZ_1Z_2}{3DKT} K\Lambda_\infty f(x) \quad \ldots (3)$$

where Z_1 and Z_2 are the ionic charges. K is some proportionality constant and $f(x)$ is a complicated function of frequency.

Also it has been shown that the electrophoretic contribution Λ_{II} is given by (Dole 1935)

$$\Lambda_{II} = \frac{e^2(n_1Z_1+n_2Z_2)}{6\pi\eta} \frac{1000}{C} \frac{K}{9\times 10^{11}} \quad \ldots (4)$$

is independence of frequency. Thus

$$\Delta\Lambda_{II} = 0$$

It therefore follows that

$$\Delta\Lambda = \Delta\Lambda_I$$
$$= af'(x)$$

where a is a constant independent of frequency. This shows that the variation in the conductance $\Delta\Lambda$ depends upon the dependence of $f(x)$ on frequency. An experimental study of the conductance with frequency will therefore lead to the study of the dependence of $f(x)$ on frequency

In the present study a marked maximum was observed in the vicinity of 4 MHz which shows that in this frequency range, the tendency of relaxation of the ionic atmosphere does not exist and ions in the electrolytic medium contribute freely. It has been shown earlier by Agarwal & Bhatnagar (1975, 1976) that one of the principal reasons for the ultrasonic effect on the conductance of electrolytic solution has been the fact that the propagation of ultrasonic wave retards the growth of ionic atmosphere around an ion in motion. The present studies further confirms this view and show that at this particular frequency of 4 MHz the ionic atmosphere is not formed.

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